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I, CAROLINE CLAIRE BROOKE, M.A.(prof.), Technical Translator, of c/o Priory Translations Limited, 11, Magdalen Street, Colchester, Essex, England, hereby state:

THAT I am well acquainted with the French and English languages.

THAT I translated the document identified as PCT Patent Application No. PCT/FR03/002499 filed on 8th August 2003, from French into English;

THAT the attached English translation is a true and correct translation of PCT Patent Application No. PCT/FR03/002499

to the best of my knowledge and belief; and

THAT all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true and further, that these statements are made with the knowledge that wilful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code

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"Method for opening carbon nanotubes at the ends thereof and applications"

The present invention relates, in a general way, to the post treatment of carbon nanotubes and their applications. In particular, the present invention is aimed at a method for opening carbon nanotubes at the ends thereof and more specifically multiwall carbon nanotubes.

Most methods of synthesis produce carbon nanotubes with closed ends which can, for example, cause the inclusion of impurities originating from the reaction medium in the central channel of the nanotube. This occurs, in particular, during the catalytic syntheses of carbon nanotubes. Moreover, when the nanotubes are initially open, they can also close again during post-treatments at high temperature.

The benefit of having open carbon nanotubes is firstly the possibility of filling their central channel with numerous species in particular conductive species (metals, conductive polymers etc.) so as to produce conductive nanowires for applications in nanoelectronics. The filled carbon nanotubes also prove to be of increasing interest in catalytic applications, and for storing energy. Moreover, hollow carbon nanotubes can prove to be excellent reservoirs for gas, such as hydrogen, natural gas, etc.

It is now well known that the presence of topological faults is necessary in order to close the graphene planes at the ends of the carbon nanotubes. According to Euler's law, six pentagons are necessary to ensure the closing of the carbon nanotubes at each end. These regions of tension are of course the most useful sites for the addition

reactions, in particular on the doubles bonds connecting a pair of pentagons.

Among the methods proposed for opening nanotubes, the following are mentioned: chemical oxidation by strong oxidizing agents in liquid phase (nitric acid, sulphuric acid or a mixture of these two acids, potassium permanganate, etc.), the reactions in gaseous phase under an air flow at temperatures varying from 500°C to 700°C and recently, impact grinding in particular in order to cut and shorten the nanotubes or also sonication.

Oxidation under air or oxygen is not as selective. These treatments lead to a significant loss of material and the external graphene planes are often seriously damaged due to the uncontrollable nature of the reaction.

Other documents have recommended using CO_2 at 850°C but at such temperatures, which are close to the conditions generally used for activating carbonaceous materials, the yields of open nanotubes are very low, the mass loss is very significant and the outer layers of graphene are badly damaged.

The oxidation is much more homogeneous when the carbon nanotubes are dispersed in an oxidizing solution. For example, the carbon nanotubes obtained by decomposition of acetylene at 600°C on cobalt particles supported by zeolites often contain carbonaceous impurities and have closed ends. It is thus possible to carry out an attack with potassium permanganate both in order to partially eliminate these impurities by oxidation and to open a part of the ends of the carbon nanotubes.

However, once again, the results in terms of efficiency and selectivity prove to be clearly inadequate.

The inventors have found that these drawbacks could be overcome by subjecting nanotubes to two distinct oxidation stages, carried out under specific conditions.

The purpose of the invention is thus to provide a method allowing the opening of carbon nanotubes to be achieved rapidly and effectively, while preserving their morphology, their quality, and with reduced losses.

Thus, the method for opening carbon nanotubes according to the invention, is characterized in that it comprises two oxidation stages, the first in liquid phase in a concentrated acid, the second in gaseous phase.

The oxidation stage in liquid phase thus allows open nanotubes to be obtained directly. Moreover, this provides the advantage of making most of the residual metal impurities trapped at the ends accessible, for example following syntheses carried out in the presence of a catalyst.

The random carbon appearing during the oxidation reaction in liquid phase is eliminated during the course of the second stage in gaseous phase.

Advantageously, the carbon nanotubes are multiwall carbon nanotubes.

More particularly, the concentrated acid is nitric acid.

Preferably, the concentrated nitric acid is used in excess.

Satisfactory results are thus obtained with 1 g of carbon nanotubes in 0.5 litres to 2 litres of concentrated HNO_3, in particular HNO_3 at 60%-75% by weight, in particular 1 litre of nitric acid at a concentration of the order of 68-70% by weight.

According to a particular embodiment of the invention, this oxidation stage is carried out at reflux, under stirring.

Advantageously, the heating at reflux will last from 30 to 50 minutes, in particular approximately 35 minutes.

For the purposes of purification, an additional oxidation stage in gaseous phase is carried out, at low temperature.

It is more particularly this stage which allows elimination by controlled oxidation of the random carbonaceous structures originating from the opening of the ends of the carbon nanotubes during the stage of opening by oxidation in liquid phase.

Advantageously, a particular embodiment of this stage consists of a treatment of approximately 1 to 2 hours, in particular under CO_2 at 500 to 600°C, in particular from 500 to 550°C and particularly 525°C, for 1 hour to 1 hour 40 minutes.

More particularly also, the method according to the invention is used with a linear velocity of said carbon dioxide of 40 to 100 cm/min, in particular of 50 to 70 cm/min, in particular of the order of 60 cm/min.

Advantageously, the method according to the invention comprises between said first oxidation stage in liquid phase and said second oxidation stage in gaseous phase, an intermediate stage of filtration and washing of the open nanotubes, in particular with distilled water. The method according to the invention can comprise an additional stage of treatment with hydrochloric acid in order to eliminate any metallic particles, initially trapped in the central channel, and released during the opening of the nanotubes.

The implementation of the above provisions, combining a reaction in liquid phase followed of a reaction in gaseous

phase, allows yields of open nanotubes of at least 90% to be obtained, without deterioration of the surface of the nanotubes and the purity which remains at levels higher than 97%.

The effectiveness of the invention will be better understood on reading the following detailed example with reference to the figures in which:

- Figure 1 represents an image obtained by scanning electron microscopy (SEM) of carbon nanotubes after a HNO_3 + CO_2 treatment according to the invention,

- Figure 2 represents a picture obtained by transmission electron microscopy (TEM) of carbon nanotubes after a HNO_3 +CO_2 treatment according to the invention,

- Figure 3 represents a TEM picture (fringe mode of a CO_2 network) of an open end of a carbon nanotube after a treatment according to the method of the invention, and

- Figure 4 represents adsorption-desorption isotherms of nitrogen at 77K of the carbon nanotubes before (full thick curve) and after implementation of the method according to the invention (dotted curve).

The method of the invention was optimized on multiwall carbon nanotubes synthesized by decomposition of acetylene at 600°C on solid solutions of $Co_xMg_{(1-x)}O$.

During a first stage, the carbon nanotubes are dispersed in the concentrated nitric acid and oxidized at reflux (130°C) for 35 minutes under continuous stirring (1 g of nanotubes in 1 litre of acid at 69% by weight). Then, the mixture is filtered, then the solid is washed with distilled water until a neutral pH of the filtrate is obtained. This first oxidation stage allows the opening of the tubes.

Then a gentle oxidation is carried out using a current of CO_2 at low temperature. This reaction is based on the Boudouard reaction ($C+CO_2 \rightarrow 2CO$ (ΔH = +159kJ/mole).

Carbon nanotube powder is placed in a quartz crucible equipped with a porous sintered glass disc allowing a rising flow of CO_2 to be introduced, at a linear velocity rate of 60 cm/min, at 525°C.

The reaction is carried out for approximately 60 to 100 minutes. A selective oxidation of the random carbon nanostructures which are produced during the first oxidation reaction is obtained.

The accumulated mass loss remains less than 50%.

The use of a scanning electron microscope (Hitachi S 4200) allows the quality of the samples of nanotubes to be evaluated (Figure 1).

Observation by TEM at 200 kV (Philips CM20) shows the effectiveness of this method with regard to the opening of the nanotubes at the ends (Figures 2 and 3). For this observation, the samples are subjected to a sonication in anhydrous ethanol and a droplet is placed on a copper grid covered with a carbon film.

The porous texture of the carbon nanotubes is characterized by the adsorption of nitrogen at 77°K (Micrometrics, ASAP 2000). Before the adsorption experiments, the samples are degassed at 350°C (10^{-6} mbar) for 12 hours.

After the opening, another heat treatment can be carried out at high temperature, at 1600-2800°C, for several hours, under nitrogen, in order to graphitize the aromatic layers of the walls and to allow the sublimation of the metallic Co.

The diameter of the tubes reduces slightly after the oxidation treatment and the rate of opening is greater than 90% (Figure 2; the arrows show open tubes). The quality of the samples is not effected by the opening treatment and the content of nanotubes is greater than 97%.

The TEM observations in fringe mode of a 002 network show that the walls are not damaged (Figure 3).

The carbon nanotubes used are very tangled. The adsorption isotherm of nitrogen at 77K is of type IV, characteristic of a mesoporous swelling solid (Figure 4). Their BET surface is 220 m^2/g and the mesoporous volume is very large (approximately 1 cm^3/g), with a BJH diameter of the order of 15 nm which corresponds to the menisci defined by the tangle of nanotubes. After opening the ends according to the invention, the mesoporous volume increases up to approximately 1.6 cm^3/g. The BET surface is then of the order of 300 m^2/g, which demonstrates the benefit of these nanotubes for the storage of energy or gas.

The above method is applied to nanotubes having external diameters of 7 to 25 mm approximately, but can be applied to nanotubes of greater diameters by adjusting the treatment time with nitric acid and with CO_2.

This method can of course be used with carbon nanotubes other than those obtained by catalytic methods.

The opening of carbon nanotubes with very high cristallinity, in particular those which are synthesized by vaporization of graphite, will require longer reaction times.

The method according to the invention is thus effective in the context of opening carbon nanotubes. More particularly, the method according to the invention is applied to the opening of multiwall carbon nanotubes.

More particularly, the method according to the invention is applied to multiwall carbon nanotubes with an external diameter comprised between 7 and 25 nm.

Yet more particularly, the multiwall carbon nanotubes to which the method according to the invention is applied are obtained by the decomposition of acetylene at 600 °C on a solid solution $Co_xMg_{(1-x)}O$.

All the thus-treated and open carbon nanotubes will prove to be of great economic and industrial benefit in particular in their use for the production of conductive nanowires, for the storage of energy, for the storage or filtration of gasses and/or for the production of a catalyst support.